

Method for Producing Metallic Flat Wires or Strips with a Cube Texture

5

Field of the Invention

The invention relates to the field of materials science and to a method for producing metallic flat wires or strips with a cube texture that can be used, for example, as a base for physical-chemical coatings having a high-grade microstructural orientation.

- 10 The texture is hereby used as the basis for crystallographically oriented growth of the deposited layers on the substrate. Such bases are suitable, for example, as substrates for metallic or ceramic coatings as used in the field of high-temperature superconductivity. Such substrate strips for coated superconductors may be used in superconducting magnets, transformers, motors, tomography instruments, or
15 superconducting current paths, i.e., cables. Such textured metal strips may also be used as magnetic materials, such as highly permeable nickel-iron alloys, for example.

Prior Art

20

It is known that polycrystalline metals having cube face-centered lattices, such as copper, nickel, gold, and under certain conditions, silver, after a previous intense cold forming may form a pronounced texture having a cubic layer in the subsequent recrystallization by rolling of sheets or flat strips (G. Wassermann: *Texturen metallischer Werkstoffe [Textures of Metallic Materials]*, Springer, Berlin, 1939; H. Hu et al.: *Trans. ASM* 224 (1962) 96-105). The underlying studies (W. Köster: *Z. Metallkde.* 18 (1926) 112-116) as well as the continuing investigations (R. D. Doherty et al.: *Mater. Sci. Eng.* A257 (1998) 18-36) were carried out using strip mill rollers followed by annealing.

25

In this manner, by rolling under the conditions of plane strain deformation and subsequent annealing, textured metal strips, in particular nickel and silver strips, are

currently used as a base for metallic coatings, ceramic buffer layers, and ceramic superconductor layers (A. Goyal et al.: U.S. Patent 5,741,377, April 21, 1998). The suitability of such metal strips as substrate materials depends primarily on the achievable degree of texturing, and the quality thereof directly on the surface.

5

In addition to the influences of chemical alloys on the texture quality, the formation of the recrystallization cube texture is above all linked to specific mechanical requirements for forming techniques. A high minimum degree of forming is indispensable in cold rolling, a fine-grained starting structure of the shaped article 10 being advantageous. The minimum degree of forming for copper is 82% (O. Dahl, F. Pawlek: Z. Metallkde. 28 (1936) 266-271). To achieve high-grade texturing, however, significantly higher degrees of forming are employed which sometimes involve greater than 99% reduction in thickness. This manufacturing technology requiring 15 very complex forming techniques is currently put up with, since alternative techniques have not been seen in decades. Therefore, in actual practice forming processes other than rolling currently do not play a role in the production of metal strips with a cube texture.

Recently, however, it has been demonstrated that the forming of strip materials using 20 a drawing process with subsequent annealing can also produce a cube texture (J. Eickemeyer, D. Selbmann, R. Opitz, B. de Boer, B. Holzapfel, L. Schultz: 8. Saxon Symposium in Shaping Technology, December 4-5, 2001, TU Bergakademie Freiberg/Sa., pages. 99-106). This procedure has thus far not become established in practice.

25

There is no universally valid theory concerning the effects of strain and deformation states on the formation of forming and annealing textures of metals, or in particular for nickel, copper, gold, and silver. Therefore, it is not possible to reliably estimate the effectiveness of a forming process for the formation of the shaped and annealed 30 textures. In addition, the friction conditions between the shaped piece and the forming tool also influence the texture formation in strips, in particular thin strips, in a manner which heretofore has not been predictable.

With the growing interest in substantially ideal annealed textures for the use of strips as very long, quasi-monocrystalline substrates (superconducting layer conductors), at the same time there is the requirement for the most perfect texture possible, not only in the strip interior, but in particular on the surface of such coating bases. For
5 this reason, all influences which may interfere with the texture formation are to be evaluated critically and avoided if possible. This applies not least of all to the optimum process conditions for material forming, which thus far have essentially been limited to the influencing variables for the rolling of strips and sheets.

10

Explanation of the Essence of the Invention

The object of the invention is to provide a method for producing metallic flat wires or strips with a cube texture, by means of which the products have a high-grade cube
15 texture after the last forming step and the final annealing treatment.

The object is attained by the invention as stated in the claims. Further developments are the subject of the subordinate claims.

20 In the method according to the invention for producing metallic flat wires or strips with a cube texture, a material based on nickel, copper, gold, or silver is processed into a wire having an essentially circular cross section by means of a cold drawing method with high-grade forming over multiple drawing stages, achieving a total cross-sectional reduction $\epsilon_g \geq 75\%$ or a logarithmic deformation $\varphi_g \geq 1.4$. The wire is
25 then further processed by means of further forming and annealing methods into a metallic flat wire or a strip with a cube texture and having a width that can be adjusted in a defined manner, the defined width being determined and adjusted by means of the wire cross section and the degrees of forming of the further forming steps for the wire.

30

The cold drawing method advantageously is implemented with a total cross-sectional reduction of $\epsilon_g \geq 90\%$ or a logarithmic deformation of $\varphi_g \geq 2.3$.

It is likewise advantageous to implement the cold drawing method as slip drawing by means of drawing dies having drawing angles $2\alpha = 2^\circ - 20^\circ$, drawing angles of $2\alpha \leq 12^\circ$ being even more advantageous.

- 5 Furthermore, it is advantageous to carry out the cold drawing method in respectively alternating drawing directions (reversibly).

It is also advantageous to omit an intermediate treatment of the wire before the further forming and annealing methods.

10

As starting material for the production of the metallic flat wire or strip, the method according to the invention uses metallic base materials which tend to form the cube texture after cold forming and subsequent recrystallization. These include metallic materials with cube face-centered lattices, such as nickel, copper, gold, and, under 15 certain conditions, silver, as well as some of the alloys thereof.

According to the invention, these metallic base materials are processed by a high-grade cold drawing to produce a wire material having an essentially circular cross section. These wires are further processed by the methods, known *per se*, of roll drawing using feely rotatable rollers, or drawing through drawing jaws arranged in parallel, or rolling to produce a metallic flat wire or a metallic strip, the cube texture being formed during the subsequent final recrystallization annealing known *per se*.

In the scope of the present invention, metallic flat wires are understood to mean 25 articles produced from wires by means of cold forming, the width and thickness being primarily determined by the starting wire diameter and the degree of forming employed.

Metallic strips are understood to mean articles produced from precursor products by 30 cold forming, the strip width being obtained by longitudinal division of wider products.

The high-grade cold drawing is carried out first by drawing the starting materials through drawing dies as commonly used in wire manufacturing. The subsequent

forming may be performed by rolling to produce strips, or by drawing of strips by use of rolling tools or drawing jaws.

Cold drawing as slip drawing through drawing dies is advantageously performed by use of drawing dies having drawing angles between 2° and 20° , and particularly advantageously with drawing angles $\leq 12^\circ$. Cold drawing of the wire may thereby be carried out in the same direction (unidirectionally), or advantageously with respectively alternating drawing directions (reversibly).

Furthermore, the method according to the invention requires no intermediate treatments of the wire after drawing of the wire and before the further forming into metallic flat wires and metallic strips, which offers technological benefits.

The method according to the invention, using cold drawing to produce a wire and further forming into a flat wire or strip and final annealing, for comparable reductions in thickness achieves at least the relative degree of texture of the cube layer as that resulting from the use of the cold rolling used heretofore, as well as from the cold drawing using rolling tools or drawing jaws. The intensive wire drawing results in a structural state that is particularly favorable for forming the subsequent recrystallization cube texture.

The primary advantage of the novel method is that, as a result of the adjustment of defined wire diameters and the adjustment of the overall degree of forming in the subsequent forming steps for the wire, the width of the finished metallic flat wires or metallic strips becomes adjustable without the longitudinal division of wide strips which otherwise would be necessary. In addition, there is no complex edge processing, so that the equipment for both longitudinal division and edge processing may be omitted in the assembly line. At the same time, the method operates without material losses, which necessarily occur as the result of cutting edge strips, and without metal-cutting products, which are unavoidable in edge processing. Technological steps are thereby omitted which also tend to consistently impair the surface quality of the sensitive strips.

Although the wire drawing method is a well-known forming method, its influence on the forming and annealing textures in metallic flat wires or metallic bands produced from wires has not been investigated heretofore.

- 5 The not unfavorable influence of wire drawing on the production of metallic flat wires or metallic strips having a cube texture is surprisingly revealed for specialized treatments, such as achieving a high-grade cube texture. This is quite unexpected for the reason that drawing textures, as fiber textures, are fundamentally different from rolling textures, and a positive influence in terms of the sought recrystallization
10 cube layer, which is known to result from the rolling texture of certain cube face-centered metals and their alloys, cannot be assumed. Even the non-homogeneous strain and deformation state, which is present in the processing of round wires to flat wires or strips over a wide dimensional range, surprisingly has no disadvantages for the end product having a cube texture.

- 15 When the method according to the invention is used for the production of substrate bands or strips for magnetic applications, a more effective manufacturing is thus technically possible at equivalent or improved product quality. This inevitably results in savings in energy and labor expenditures, as well as cost savings for specialized
20 equipment which would otherwise be necessary for longitudinal division and edge processing.

- 25 The melt metallurgical production of the metals and alloys to be textured is preferably carried out by casting into a copper mold. As an alternative to melt metallurgical production, powder metallurgical production using hot and cold isostatic pressing may also be appropriate for the starting material.

- 30 Before the subsequent conventional heat forming is begun, the metallurgically produced cast or pressed bodies may acquire an advantageous starting structure by homogenization annealing, and the grain size may be adjusted in a controlled manner for the final intensive cold forming. From the standpoint of good cold formability, the degree of heat forming as well as the temperature and duration of annealing may be easily optimized in the subsequent process by one skilled in the

art. The annealing atmosphere for the recrystallization advantageously is reducing or inert. The annealing temperatures and times tend towards changed values with increasing alloy content, and likewise may be easily adjusted by one skilled in the art.

5

Compared to other known approaches, the fundamental difference in the approach according to the invention is that a wire having an essentially circular cross section may also be used as starting product for the flat wire or strip production without resulting disadvantageous effects on the cube texture in the flat wire or strip to be ultimately produced. This would not have been expected according to the prior art.

10 Depending on the type of wire, the drawing and annealing textures in wires are fiber textures, and consequently are characterized by a single preferred direction, the wire axis. It was therefore surprising that a high-grade drawn wire having a fiber texture could be prepared by means of comparatively minor subsequent flat forming to form
15 a biaxial recrystallization cube texture.

Most Advantageous Approach for Carrying Out the Invention

The invention is explained in greater detail below, with reference to examples.

20

They show:

Fig. 1: A structural image obtained by EBSD, and the degree of texture of a 82-
25 μm thick nickel-iron strip (Ni53Fe47) produced by unidirectional roll drawing from a diameter of 1.25 mm ($\varepsilon = 87.9\%$), after the starting wire was drawn from $\varnothing 20 \text{ mm}$ to $\varnothing 5 \text{ mm}$ ($\varepsilon = 93.75\%$), and following an intermediate annealing was further drawn to $\varnothing 1.25 \text{ mm}$ ($\varepsilon = 93.75\%$).

Example 1

30 A circular rod made of Ni53Fe47 alloy is drawn in the conventional manner by rod or wire drawing in multiple stages, from a diameter of 20 mm to a wire having an essentially circular cross section of 5 mm in diameter (1st overall reduction of $\varepsilon_g =$

93.75%). After a recrystallization annealing at 850°C, further cold drawing results in a diameter of 1.25 mm (2nd overall reduction of $\varepsilon_g = 93.75\%$). This wire is then further processed by means of unidirectional roll drawing, with a cross-sectional reduction of $\varepsilon_g = 87.4\%$, to a flat wire having a width of 1.89 mm and a thickness of 82 μm .

5 Texture annealing at 1100°C over a period of 60 minutes results in a high-grade recrystallization cube texture which constitutes a share of 94.3% in the structure (Fig. 1), 93.1% of all grain boundaries being small-angle grain boundaries with a misorientation < 10° (white in Fig. 1). In conventional procedures for continuous strip forming of flat products, such a texture quality is not achieved until the reduction in

10 strip thickness is greater than $\varepsilon_g = 99\%$. Further machining of the flat wire obtained is not necessary.

Example 2

A circular rod made of Ni53Fe47 alloy is drawn in the conventional manner by rod or wire drawing in multiple stages, from a diameter of 20 mm to a wire having an essentially circular cross section of 5 mm in diameter (1st overall reduction of $\varepsilon_g = 93.75\%$). After a recrystallization annealing at 850°C, further cold drawing results in a diameter of 1.25 mm (2nd overall reduction of $\varepsilon_g = 93.75\%$). This wire is then further processed by means of reversible roll drawing, with a cross-sectional reduction of $\varepsilon_g = 87.9\%$, to a strip having a width of 1.86 mm and a thickness of 77 μm . Texture annealing at 1100°C over a period of 60 minutes results in a high-grade recrystallization cube texture which constitutes a share of 91.3% in the structure, 92.8% of all grain boundaries being small-angle grain boundaries (misorientation < 10°). In conventional procedures for continuous strip forming of flat products, such a texture quality is not achieved until the reduction in strip thickness is greater than $\varepsilon_g = 99\%$. Further machining of the flat wire obtained is not necessary.

Example 3

30 A circular rod made of Ni53Fe47 alloy is drawn in the conventional manner by rod or wire drawing in multiple stages, from a diameter of 20 mm to a wire having an essentially circular cross section of 1.25 mm in diameter (1st overall reduction of

$\varepsilon_g = 99.6\%$). This wire is then further processed by means of reversible roll drawing, with a cross-sectional reduction of $\varepsilon_g = 87.9\%$, to a strip having a width of 1.83 mm and a thickness of 80 μm . Texture annealing at 1100°C over a period of 60 minutes results in a high-grade recrystallization cube texture which constitutes a share of 5 91.6% in the structure, 83.6% of all grain boundaries being small-angle grain boundaries (misorientation < 10°). Further machining of the strip obtained is not necessary.

Example 4

10 A circular rod made of Ni53Fe47 alloy is drawn in the conventional manner by rod or wire drawing in multiple stages, from a diameter of 20 mm to a wire having an essentially circular cross section of 5 mm in diameter (1st overall reduction of $\varepsilon_g = 93.75\%$). After a recrystallization annealing at 850°C, further cold drawing results in a diameter of 1.25 mm (2nd overall reduction of $\varepsilon_g = 93.75\%$). This wire is 15 then further processed by means of reversible roll drawing, with a cross-sectional reduction of $\varepsilon_g = 82.2\%$, to a strip having a width of and a thickness of 97 μm . Texture annealing at 1100°C over a period of 60 minutes results in a high-grade recrystallization cube texture which constitutes a share of 82.9% in the structure, 61.9% of all grain boundaries being small-angle grain boundaries (misorientation < 20 10°). Further machining of the strip obtained is not necessary.

Example 5

A nickel wire having an alloy content of 5 atomic-% tungsten is drawn in multiple stages from a starting diameter of 5 mm to a diameter of 1 mm ($\varepsilon_g = 96\%$). The wire 25 is then cold rolled, without intermediate treatment, into a flat wire having final dimensions of 1.9 mm width and 60 μm thickness. The flat wire is finally subjected to a heat treatment at 1100°C over a period of 1 hour, forming a sharply defined cube texture as used for bases for coating with epitactically grown layers.